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Growth, Characterization and Device Development in Monocrystalline Diamond Films

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<p>Approved for Public Release; Distribution Unlimited</p> <p>Photoemission and field emission from p-type natural diamond crystals are dependent on the surface termination. Hydrogen termination results in a negative electron affinity (NEA) while O and adsorbate-free surfaces exhibit positive electron affinities. Thin metal layers can induce an effective NEA which can be modeled in terms of the metal workfunction and the metal-diamond Schottky barrier. NEA surfaces of p-type diamond are shown to exhibit emission with lower voltages. Nitrogen-doped films exhibited very high threshold fields, indicating different processes for insulating and p-type diamond. Current-voltage characteristics of tip-shaped molybdenum field emitters were investigated before and after coating with diamond or graphite powders. Stable emission was observed only after annealing and formation of a conductive Mo carbide layer at the metal-coating interface. Both coated emitters displayed enhanced emission and a reduction by a factor of two in the "turn-on" voltages as compared to the uncoated emitters. For the graphite coated emitter, the enhancement was attributed to an increase in the field enhancement factor due to the coating morphology. Roughening of the Mo-diamond interface via carbide formation during the annealing step is presumed to have caused the enhanced emission for the diamond coated emitter. The transmission probabilities for the Mo-diamond and diamond-vacuum interface were calculated, using the WKB method, based on an emission mechanism from the intrinsic diamond's conduction band minimum. With a field locally enhanced to 10^8 V/cm, the transmission probability for the diamond-vacuum interface was 10^8 times larger than that of the Mo-diamond interface. This evaluation confirmed that the electron affinity of the diamond surface is not a governing factor in the emission from intrinsic diamond.</p>				
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Table of Contents

I.	Introduction	1
II.	Electron Emission from Diamond Films and Surfaces <i>R. J. Nemanich, P. K. Baumann, A. T. Sowers, and B. L. Ward</i>	2
III.	Electrical Characterization of Diamond and Graphite-coated Mo Field Emitters <i>M. T. McClure, R. Schlessner, B. L. McCarson and Z. Sitar</i>	7
IV.	Distribution List	16

I. Introduction

Diamond as a semiconductor in high-frequency, high-power transistors has unique advantages and disadvantages. Two advantages of diamond over other semiconductors used for these devices are its high thermal conductivity and high electric-field breakdown. The high thermal conductivity allows for higher power dissipation over similar devices made in Si or GaAs, and the higher electric field breakdown makes possible the production of substantially higher power, higher frequency devices than can be made with other commonly-used semiconductors.

In general, the use of bulk crystals severely limits the potential semiconductor applications of diamond. Among several problems typical for this approach are the difficulty of doping the bulk crystals, device integration problems, high cost and low area of such substrates. In principal, these problems can be alleviated via the availability of chemically vapor deposited (CVD) diamond films. Recent studies have shown that CVD diamond films have thermally activated conductivity with activation energies similar to crystalline diamonds with comparable doping levels. Acceptor doping via the gas phase is also possible during activated CVD growth by the addition of diborane to the primary gas stream.

The recently developed activated CVD methods have made feasible the growth of polycrystalline diamond thin films on many non-diamond substrates and the growth of single crystal thin films on diamond substrates. More specifically, single crystal epitaxial films have been grown on the {100} faces of natural and high pressure/high temperature synthetic crystals. Crystallographic perfection of these homoepitaxial films is comparable to that of natural diamond crystals. However, routes to the achievement of rapid nucleation on foreign substrates and heteroepitaxy on one or more of these substrates has proven more difficult to achieve. This area of study has been a principal focus of the research of this contract.

At present, the feasibility of diamond electronics has been demonstrated with several simple experimental devices, while the development of a true diamond-based semiconductor materials technology has several barriers which a host of investigators are struggling to surmount. It is in this latter regime of investigation that the research described in this report has and continues to address.

In this reporting period, (1) photoemission and field emission from adsorbate-free and H- and O-terminated diamond surfaces and (2) current-voltage characteristics of uncoated and diamond or graphite coated, tip-shaped Mo field emitters have been determined. The following section is self-contained in that it presents an introduction, the experimental procedures, results and discussion, summary and indications of future research for the given research thrust.

II. Electron Emission from Diamond Films and Surfaces

A. Introduction

The processes of photoemission and field emission of electrons have similarities and differences. Electrons in the photoemission process are excited into the conduction band and depending on the energetics and surface properties, may be emitted into vacuum. Electrons for deep UV excitation such as HeI at 21.2 eV may be excited more than 10 eV above the conduction band minimum and certainly some electron emission will be observed. The electrons that quasi thermalize to the conduction band minimum will only be emitted if the surface exhibits a negative electron affinity (NEA). For an n-type semiconductor with available electrons in the conduction band, the field emission would exhibit a barrier equal to the electron affinity, but the electrical resistance could also limit the processes.

This report summarizes studies of photoemission and field emission from p-type diamond single crystal samples. Moreover, field emission results from nitrogen-doped diamond films are discussed. The N doping is expected to produce films with a deep level at 1.7 eV from the conduction band and, hence allow electron supply to the conduction band.

Ultraviolet photoemission spectroscopy (UPS) can be used to measure the electron affinity of a semiconductor, and to indicate if the surface exhibits a NEA [1-3]. Unfortunately, UPS cannot determine the vacuum level for a system with a NEA. Furthermore, UPS can be used to measure Schottky barrier heights of thin metal layers on p-type semiconductors. Field emission measurements integrate the effects of injecting electrons into the semiconductor, transporting the carriers through the bulk and emission from the surface. However, a bias is applied between a metal anode and the sample to facilitate these measurements, and the emission current is detected.

Prior results have established a NEA for hydrogen-terminated, p-type diamond surfaces. For field emission from p-type diamond, electrons must be excited into the conduction band or the emission could originate from electrons in the valence band [4].

The configuration for a thin metal layer on diamond may be modeled as two separate interfaces, namely the vacuum-metal and metal-diamond interface [5-9]. Electrons in very thin metal layers could travel through the metal layer without scattering. The equation below gives an expression for the effective electron affinity for a thin metal overlayer on a semiconductor.

$$\chi_{\text{eff}} = (\Phi_m + \Phi_b) - E_g \quad (1)$$

With the bandgap of diamond $E_g = 5.47$ eV, the metal workfunction, Φ_m , and the measured Schottky barrier height, Φ_b , the effective electron affinity can be calculated. Thus the Schottky barrier height of the metal-diamond interface plays a critical role in determining the relationship of the diamond conduction band and the vacuum level and if the structure exhibits a NEA.

B. Experimental Procedure

Natural type IIb p-type (boron doped) semiconducting single crystal diamonds of (100), (111) and (110) crystals were employed. Typical resistivities were 10^4 $\Omega\text{-cm}$. Surfaces were prepared using an electrochemical etch. The surface treatments, photoemission and field emission measurements were completed in a UHV system comprised of several interconnected chambers that included capabilities for annealing, H plasma cleaning, metal deposition, angle-resolved ultraviolet photoemission spectroscopy (ARUPS), moving probe field emission, Auger electron spectroscopy (AES) and low energy electron diffraction (LEED).

C. Results

Single Crystal P-type Diamond Photoemission. First considered were the properties of the diamond (100), (111) and (110) surfaces. Diamond (100) samples annealed to 500°C exhibited a 1×1 LEED pattern and the AES indicated oxygen termination. An 1150°C anneal or an H plasma exposure resulted in a 2×1 reconstructed surface and the removal of oxygen according to AES. The UPS results indicated that the surfaces annealed to 500°C and 1150°C showed a positive electron affinity of 1.45 eV and 0.75 eV, respectively while a NEA was induced by the H plasma exposure.

For diamond (111) surfaces, annealing to 1150°C or exposure to a H plasma resulted in a 2×1 LEED pattern and caused the amount of surface oxygen to drop below the detection limit of the AES system. The UPS measurements indicated a positive electron affinity of ~ 0.55 eV after an 1150°C anneal and a NEA was indicated after the H plasma exposure.

A 700°C anneal or a H plasma exposure removed the oxygen from the diamond (110) surfaces according to AES, and NEA characteristics were observed in the UPS. A positive electron affinity of 0.55 eV was determined after an anneal to 1150°C.

The photoemission results for a series of thin metal layers on O terminated, H terminated and adsorbate free diamond is summarized in Fig. 1. The measured Schottky barrier heights of the different metal–diamond interfaces were plotted vs. the metal workfunction for Zr, Ti, Cu, Co and Ni. The presence of a NEA was indicated by the open and filled data points. The dashed line represents the limiting value of the Schottky barrier for which a NEA is expected for metal–diamond interfaces. Thus, a NEA was expected for data points below this dashed line and a positive electron affinity for those above. As is evident, the experimental results for the electron affinity agreed with this model except for Ni. Based on theoretical studies, it has been suggested that the measured NEA may be indicative of the presence of two configurations of Ni on the surface with different Schottky barrier heights of 0.1 eV and 0.8 eV, respectively. The model would predict that the regions with a Schottky barrier of 0.1 eV would exhibit a NEA while the other regions would exhibit a positive electron affinity.

The results also showed that metals deposited on hydrogen-terminated and adsorbate-free surfaces exhibited a similar dependence except that the Schottky barrier was slightly larger for the H terminated surfaces. In contrast, the Schottky barrier for metals on oxygen-terminated diamond was nearly constant except for Ti and Zr. These last two metals were highly reactive, and it was proposed that they displaced the oxygen from the metal diamond interface to react directly with the diamond.

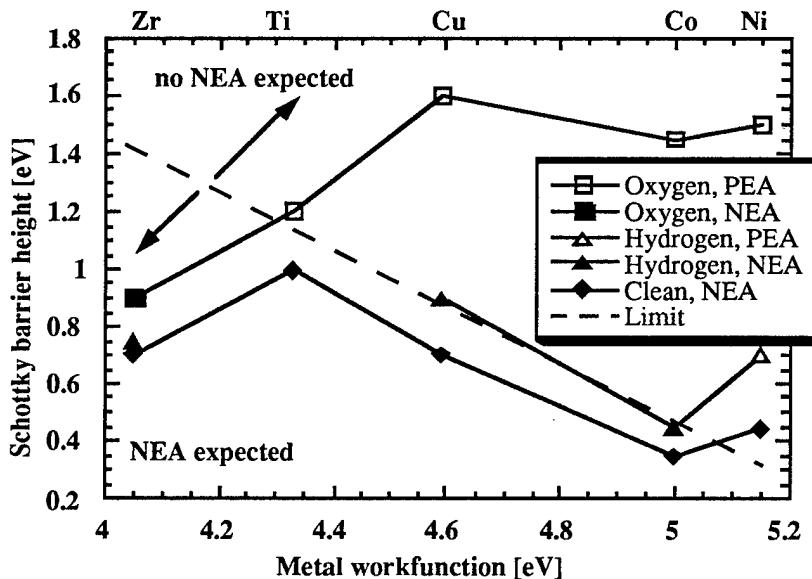


Figure 1. Summary of photoemission measurements for metal films deposited on p-type diamond. The data indicate the measured Schottky barrier for the different diamond surface termination and metal, and the open points indicate a positive electron affinity while the filled data points indicate a NEA.

Field Emission Results. Field emission measurements [10] were performed on diamond (100) and (110) samples as well as on 2 Å and 10 Å thick Zr or Co films deposited on clean, hydrogen or oxygen terminated diamond (100) surfaces. The measurements were used to determine the applied voltage per μm where detectable emission was observed. The voltage per μm was sometimes termed the average field. Since the measured current–voltage curves did not exhibit an absolute threshold, it was necessary to define the emission threshold voltage per μm for a specific current. In this study, a value of 100 nA was employed.

An average threshold field of 81 V/ μm was determined for the oxygen-terminated diamond (110) surface, while a field emission threshold of 25 V/ μm was observed for the hydrogen terminated C(110) surface. According to UPS measurements, oxygen-terminated diamond surfaces exhibit a positive electron affinity while hydrogenated diamond surfaces show NEA characteristics.

For both Zr and Co deposition, the lowest threshold has been obtained for the clean surface, and average values of 20 V/ μm and 30 V/ μm have been determined for Zr and Co,

respectively. The next highest values of 23 V/ μ m for Zr and 39 V/ μ m for Co were measured on the hydrogen terminated surface. Zr or Co films on clean and H-terminated surfaces also exhibited a NEA as determined from the UPS spectra. Higher threshold average field values were obtained for the Co and Zr on the oxygen terminated diamond. A value of 49 V/ μ m was determined for Zr on the oxygenated surface, and this surface still exhibited a NEA. The Co on the oxygen-terminated surface resulted in the highest average field value of 52 V/ μ m for the different metal-diamond interfaces studied. This surface exhibited a positive electron affinity.

The general trend of the results is that the threshold field decreased with decreasing electron affinity. The surfaces exhibiting a NEA also exhibited a lower field emission threshold than those with a positive electron affinity. However, it is evident that these results were suggestive that the field emission was from electrons that originated from the valence band.

Nitrogen Doped Diamond Films. Nitrogen-doped diamond films were prepared by microwave CVD using a range of different nitrogen to carbon ratios. The films were deposited on n-type Si substrates. Substrates were prepared by diamond polishing or alternatively biased enhanced nucleation was employed on chemically cleaned substrates. The surface morphology varied from well faceted domains to rough microdomains. PL showed evidence of nitrogen and the Raman showed varied amounts of diamond and sp^2 bonded carbon. Scanning electron microscopy of all samples showed charging indicating insulating character. The field emission of all samples showed average threshold fields of 80 to 150 V/ μ m. This value was essentially independent of thickness from 200nm to 5 μ m. Moreover, the average field for emission was nearly independent of the anode distance indicating that the field was applied to the surface.

While previous studies have suggested that N doping may result in low field emission because the electrons could be supplied to the conduction band, this possibility was never confirmed.

D. Conclusions

The research described in the section demonstrated a correlation of the electron emission and surface conditions for p-type single crystal diamond. The results suggested that the field emission originated from the valence band while the photoemission originated from electrons excited into the conduction band. These results indicated that for p-type diamond, the supply contacts and transport through the diamond do not substantially limit the emission.

In contrast to prior results, the measurements presented here for nitrogen doped films indicated a high field is necessary to obtain field emission. It has not yet been determined whether the emission was from electrons from the valence band, conduction band, or defect conduction mechanisms. It was evident that verification of field emission from electrons in the conduction band would be a critical aspect for future studies.

E. References

1. J. van der Weide and R.J. Nemanich, *J. Vac. Sci. Technol. B* **10**, 1940 (1992).
2. J. van der Weide and R.J. Nemanich, *Appl. Phys. Lett.* **62**, 1878 (1993).
3. J. van der Weide, Z. Zhang, P.K. Baumann, M.G. Wensell, J. Bernholc and R.J. Nemanich, *Phys. Rev. B* **50**, 5803 (1994).
4. C. Bandis, B.B. Pate, *Appl. Phys. Lett.* **69**, 366 (1996).
5. J. van der Weide and R.J. Nemanich, *Phys. Rev. B* **49**, 13629 (1994).
6. P.K. Baumann and R.J. Nemanich, *Appl. Surf. Sci.* **104/105**, 267 (1996).
7. P.K. Baumann, S.P. Bozeman, B.L. Ward and R.J. Nemanich, *J. Diam. Rel. Mat.* **6**, 398-402 (1997).
8. P.K. Baumann and R.J. Nemanich, *J. Vac. Sci. Tech. B* **15** (1997), in press.
9. P.K. Baumann and R.J. Nemanich, *J. Diam. Rel. Mat.* **4**, 802 (1995).
10. S.P. Bozeman, P.K. Baumann, B.L. Ward, M.J. Powers, J.J. Cuomo, R.J. Nemanich and D.L. Dreifus, *J. Diam. Rel. Mat.* **5**, 802 (1996).

III. Electrical Characterization of Diamond and Graphite-coated Mo Field Emitters

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Current-voltage characteristics of tip-shaped molybdenum field emitters were investigated before and after coating with diamond or graphite powders. Stable emission was observed only after annealing and formation of a conductive Mo carbide layer at the metal-coating interface. Both coated emitters displayed enhanced emission and a reduction by a factor of 2 in the "turn-on" voltages as compared to the uncoated emitters. For the graphite-coated emitter, the enhancement was attributed to an increase in the field enhancement factor due to the coating morphology. Roughening of the Mo-diamond interface via carbide formation during the annealing step is presumed to have caused the enhanced emission for the diamond coated emitter. The transmission probabilities for the Mo-diamond and diamond-vacuum interface were calculated, using the WKB method, based on an emission mechanism from the intrinsic diamond's conduction band minimum. With a field locally enhanced to 10^8 V/cm, the transmission probability for the diamond-vacuum interface was 10^8 times larger than that of the Mo-diamond interface. This evaluation confirmed that the electron affinity of the diamond surface is not a governing factor in the emission from intrinsic diamond.

A. Introduction

Diamond has attractive physical properties (e.g., high thermal conductivity, chemical inertness, and negative electron affinity with appropriate surface termination) that make it an enticing cold cathode material. For diamond to gain widespread industrial acceptance for vacuum microelectronic applications, such as flat panel displays, considerable field emission should be available at a low voltage compatible with standard IC driver electronics.

Two common methods for improving field emission device performance is modification of the geometry of the device to locally enhance the electric field at the cathode and using low work function materials [1]. Asano *et al.* [2] investigated diamond-based emitters by ion milling diamond grains deposited on a Si substrate. They proposed that the primary cause for enhanced field emission was the increased local field due to the sharpening of the diamond grains. Zhirnov *et al.* [3] explained the enhanced emission performance of needle shaped Si emitters coated with diamond using a two-step field enhancement process. They proposed that the Si needle shape enhances the local electric field and microscopic protrusions on the diamond grains contribute to a further enhancement of the electric field.

The use of low work function materials for emitters has been hampered due to the reactivity usually associated with these materials (e.g. Cs, Li, etc.). Negative electron affinity (NEA) surface has been suggested as the cause for the enhanced emission from diamond-based emitters. Zhirnov *et al.* [3] proposed that the diamond (111) NEA surface is the cause of observed low effective work function and enhanced emission characteristics for diamond-coated Si micro-emitters. It is widely accepted that a diamond cathode with an NEA surface would be a efficient field emitter.

However, whether NEA is a mandatory requirement for efficient emission at low electric fields is not clear [4, 5]. NEA has been demonstrated for p-type diamond samples via ultraviolet photoemission spectroscopy (UPS) [6, 7]. However, electron emission originates from the valence band for p-type diamond; thus, the work function is on the order of the bandgap (5.5 eV). An assumed NEA of 1 eV would lower the barrier to emission for p-type material to 4.5 eV, comparable to that of most metals. In the case of intrinsic diamond, emission occurs from the conduction band minimum [8] and the emission barrier is reduced to the electron affinity. However, for intrinsic diamond, the emission current is dependent on electron injection into the conduction band from an metallic back contact. Recent experiments and models have emphasized the importance of electron injection from the substrate into the diamond conduction band [8, 9]. They have shown that the injection barrier at the substrate-diamond interface is a more limiting factor to the emission current than the field emission barrier at the diamond-vacuum interface.

To clarify the role of NEA for substantial emission from diamond-coated emitters, a comparative study of I-V characteristics from graphite and diamond-coated Mo emitters was

performed. Graphite is a carbon material that does not feature NEA properties. Any interface chemistry between the Mo tip and the coating (e.g., the formation of a Mo_2C interlayer) possibly influencing the field emission process would be comparable for the two selected coating materials.

B. Experimental Procedure

Mo emitters were fabricated by electrochemically etching 0.125 mm diameter wire and had typical radii of curvature of 100 nm or less. Diamond powder was obtained from Amplex, Inc. and had a particle size distribution of 0–0.1 μm . The powder was nominally undoped; Raman spectroscopy evidenced no Raman active defects. The graphite powder (2–15 μm particle size, Alfa/Æsar) was first ground with a mortar and pestle to produce a smaller particle size. The carbon coatings were deposited by an electrophoretic procedure described in reference [8]. Careful timing of the process allowed deposition of 70–150 nm thick coatings.

The field emitters were mounted approximately 500 μm from a stainless steel gate electrode. A Keithley 237 high voltage source was used to bias the emitter negatively with respect to the gate, and the emitted current was measured with integrated picoammeter. The leakage current could be kept below 1 pA, and did not considerably affect the measured field emission currents.

C. Characterization of Emitters

I-V characteristics of each uncoated Mo sample was first measured as a standard for later comparison. The uncoated Mo emitter was heated in vacuum (500°C, 12 hrs., pressure: 10^{-7} Torr) to remove any atmospheric contaminants. After it had cooled to room temperature, it was transferred to the testing chamber (pressure: 10^{-9} Torr) for characterization. Following the measurements, the sample was removed from vacuum for coating.

Scanning electron microscopy (SEM) was used to determine the thickness and uniformity of the carbon films (diamond: ~150 nm and graphite: ~70 nm). The diamond coating had a coarse, particulate morphology while the graphite coating consisted of features too fine to be imaged effectively in the SEM. Presumably the coating was composed of thin sheets of graphite forming protrusions normal to the surface of the Mo tip, as evidenced by a “feathery” morphology seen in the micrographs.

After coating with either graphite or diamond, the emitters displayed large current fluctuations (up to 50%), presumably due to a poor electrical contact between the Mo substrate and the coating. Therefore, the coated samples were annealed at 500°C for more than 1 hr. (pressure: 10^{-7} Torr). The purpose of this annealing step was three-fold: (i) to remove atmospheric contaminants, (ii) to remove any Mo oxide that might have formed while the emitter was out of vacuum during the coating procedure, and (iii) to promote formation of an

interfacial Mo carbide layer to improve the electrical contact at the Mo-coating interface. Myers *et al.* [10, 11] investigated the Mo-diamond interface of similarly prepared diamond-coated emitters with transmission electron microscopy (TEM). Micrographs indicated that without any heat treatment the Mo emitter surfaces were covered with a native oxide approximately 100Å thick. After annealing in vacuum for 1 hour at 450°C, TEM micrographs indicated that a carbide layer had formed and the majority of the oxide layer had been removed. Thus, the annealing time and temperature used in this study are expected to form a conductive carbide layer and reduce the presence of an oxide layer. After annealing, the emission behavior was stable with current fluctuations of approximately 5%.

To examine the field emission characteristics from the samples, the I-V data was converted into $\ln(I/V^2)$ vs. $(1/V)$ coordinates, which express the Fowler-Nordheim equation in a linear form [12]:

$$\ln\left(\frac{I}{V^2}\right) = a\left(\frac{1}{V}\right) + b \quad (1)$$

$$a = -6.44 \times 10^7 \Phi^{3/2} / \beta, \quad b = \left(\frac{10.4}{\Phi^{1/2}} \right) + \ln\left(1.5 \times 10^{-6} \frac{\beta^2}{\Phi} A \right),$$

where the applied voltage, V [V], is linked to the measured current, I [A], through three parameters: the work function, Φ [eV], the field enhancement factor, $\beta = F/V$ [cm⁻¹], and the emitting area, A [cm²]. The Fowler-Nordheim plots for the emitters before and after the graphite and diamond coating are shown in Figs. 1 and 2, respectively. The I-V data collected from all emitters displayed a linear behavior characteristic of Fowler-Nordheim emission.

Interpretation of the slope and offset determined from the Fowler-Nordheim graph can be misleading because the structure of the nanoscale emitters deviates from the assumptions in the Fowler-Nordheim current equation. Several researchers [13-15] have developed theoretical and numerical models for a more accurate emission current equation for emitters with a small radius of curvature and semiconductor based emitters. However, the trends predicted by the Fowler-Nordheim equation (Eq. 1) are valid and the change in the emission performance after coating will be discussed in qualitative terms.

Undoubtedly, an emitter displaying enhanced emission is one that results in higher emission current for a given applied voltage compared to a reference emitter. Thus, one can easily quantify the enhancement by calculating a voltage factor as the ratio of voltage applied to the coated tip and that applied to the uncoated tip (the reference emitter) to obtain a given current:

$$\text{Voltage factor} = \left. \frac{V_{coated}}{V_{uncoated}} \right|_I. \quad (2)$$

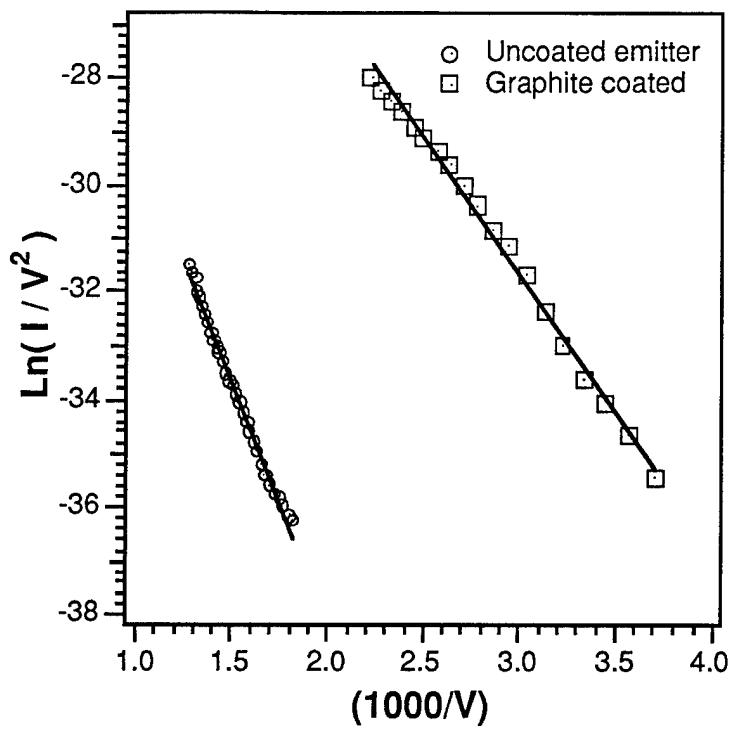


Figure 1. Fowler-Nordheim plot of I-V data collected from the graphite-coated emitter (squares) with the uncoated emitter (circles) shown for comparison.

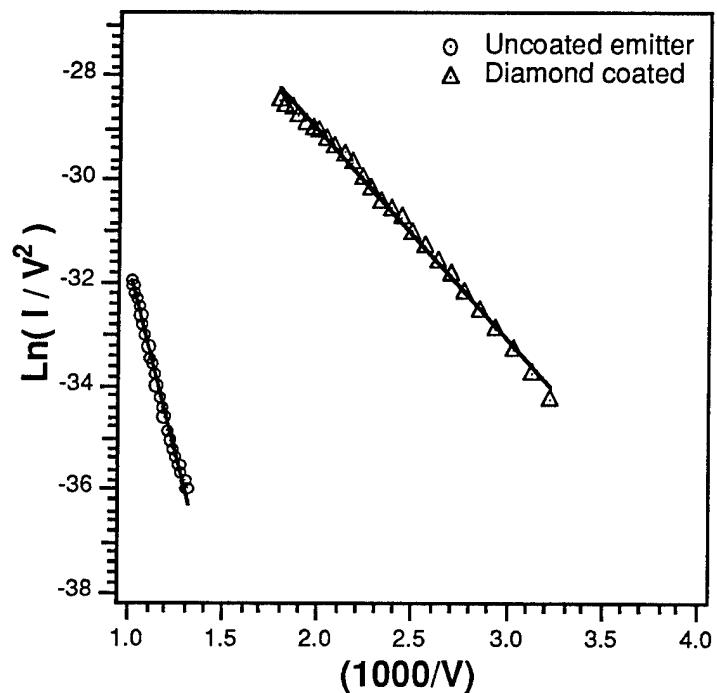


Figure 2. Fowler-Nordheim plot of I-V data collected from the diamond-coated emitter (triangles) with the uncoated emitter (circles) shown for comparison.

For example, to obtain 10 nA from a bare Mo emitter 970 V were needed; on the same emitter, this voltage decreased to 420 V after diamond coating. Thus, the voltage factor for this current was $420/970 = 0.43$. Figure 3 shows the voltage factor for the diamond and graphite-coated emitters at different currents, indicating that approximately half of the applied voltage was required for the coated emitters to obtain the same current observed prior to coating. Thus, having identified enhanced emission via the voltage factor calculation, the cause for the enhancement through the change in the physical parameters, namely β and A , after coating can be determined relative to the uncoated tip.

Graphite-coated Emitter. As indicated by the voltage factor, the graphite-coated emitter revealed an increase in emission current for the same voltage. Since the work functions of graphite and Mo are equal ($\Phi(\text{graphite}) = 4.6 \pm 0.01$ eV [16], $\Phi(\text{Mo}) = 4.6 \pm 0.2$ eV [17]), the decrease in a and an increase in b (see Eq. 1 and Fig. 1) reflect changes in the structure of the emission surface. The emission area increased by a factor of 20 and the field enhancement factor increased by almost a factor of two. Both of these changes can be attributed to the coating morphology. The morphology of the coating, which consisted of thin graphite sheets protruding normal to the Mo surface, would have increased the local field strength and exposed more surface area from which the emission occurred. Thus, the enhanced emission current observed was attributed solely to the surface topography which enhanced the local electric field.

Diamond-coated Emitter. After diamond coating, the voltage factor calculation also indicated enhanced emission behavior compared to the uncoated Mo emitter. The slope of the

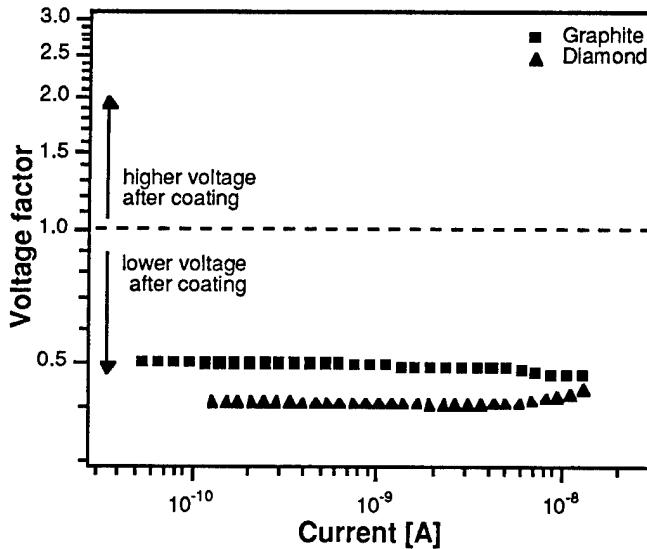


Figure 3. Voltage factor for emission current from the graphite and diamond-coated Mo emitters. The voltage factor compares the voltage required after coating to achieve the same emission current as before coating.

Fowler-Nordheim plot, a , decreased by more than a factor of 3 and the offset, b , decreased from -17.7 to -21 after coating (see Fig. 2). A decrease in the slope of the Fowler-Nordheim plot would signify an increase in β and/or a decrease in Φ . Local enhancement of the electric field has been suggested for diamond-coated emitters by Zhirnov *et al.* [3] and Asano *et al.* [2].

Since the slope of the Fowler-Nordheim plot depends on β and Φ , reducing the barrier height would also enhance emission. With the intrinsic diamond coating on the Mo tip, there are two interfaces present (injection and emission), and the larger barrier is expected to be the rate limiting step. Schlessler *et al.* [8] have observed a Mo-diamond barrier height of 3 eV for an intrinsic coating, which is larger than the electron affinity of the diamond emission surface, $-0.4 \leq \chi \leq 1.5$ eV [6]. Thus, the Fowler-Nordheim data need to be interpreted in terms of the injection barrier height, taken to be 3 eV in this case. Based on a conduction band emission mechanism expected for intrinsic diamond, a barrier height of 3 eV at the Mo-diamond interface would require an increase of β by about a factor of two, compared to the uncoated Mo emitter, to account for the change in slope observed in the Fowler-Nordheim graph.

Rather than relying on “tiny ultra-sharp” protrusions [3] on the diamond surface to enhance the electric field, the increase in the field enhancement factor may have arisen from changes in the Mo-diamond interface. The interface topography may have changed during the annealing process as Mo carbide regions form where the diamond grains contact the Mo tip. The reduced emission area observed from the Fowler-Nordheim data supports a limited contact area interface structure.

Comparison of Injection and Emission Barriers. As long the emission barrier is not the governing factor in the emission process, analysis of the Fowler-Nordheim data cannot determine whether or not the diamond-vacuum interface is a NEA surface. One can determine what influence a positive electron affinity surface has on the emission current by comparing the transmission probability to the Mo-diamond interface. Using the WKB approximation for a triangular barrier, the transmission probability, P , is given by [18]:

$$P = \exp \left[-\frac{4(2m^*)^{1/2}}{3\hbar} \frac{(\Phi_{BH})^{3/2}}{eF} \right], \quad (3)$$

where m^* is the electron effective mass in the material from which the electrons originate, $\hbar = (h/2\pi)$, h is Planck’s constant, Φ_{BH} is the barrier height, and F is the electric field. The injection barrier height is determined by the Schottky barrier height between Mo and diamond, $\Phi(\text{injection}) = 3$ eV [8], but the external field strength at this interface is decreased by the dielectric constant of diamond, $\epsilon = 5.6$ [19]. At the diamond-vacuum surface, the emission barrier is determined by the electron affinity. A conservative estimate for the positive electron affinity surface would be an oxygen terminated diamond surface where

$\Phi(\text{emission}) = 1.5 \text{ eV}$ [6]. The low electron effective mass in diamond ($m^* = 0.2m_0$, m_0 is the electron mass [19]) reduces the emission probability into vacuum. Our experimental conditions would produce a locally enhanced electric field on the order of 10^8 V/cm at the diamond-vacuum interface. At these conditions, the transmission probability at the emission barrier is 10^8 times greater than that at the injection barrier. Figure 4 displays the transmission probability ratio, $(P(\text{emission})/P(\text{injection}))$, over the range of our experimental conditions. One can easily observe that a positive electron affinity surface of diamond poses a negligible barrier compared to the injection barrier.

D. Conclusions

For both the graphite and diamond-coated emitters, stable and enhanced emission was observed only after annealing. The unstable emission prior to annealing was attributed to a poor electrical contact between the Mo tip and the coating. The annealing procedure would have produced a conductive Mo carbide layer and reduce the presence of an insulating Mo oxide layer. A voltage factor, the ratio of the voltage required after coating to that before coating to obtain a given current, was introduced to quantify the current increase. Both coatings displayed a voltage factor of approximately 0.5. For the graphite-coated emitter, the larger current was attributed to an increase in the field enhancement factor, β , and increased surface area due to the coating morphology. The enhanced emission current for the diamond-coated emitter was attributed to the morphology at the Mo-diamond interface. The lower barrier height

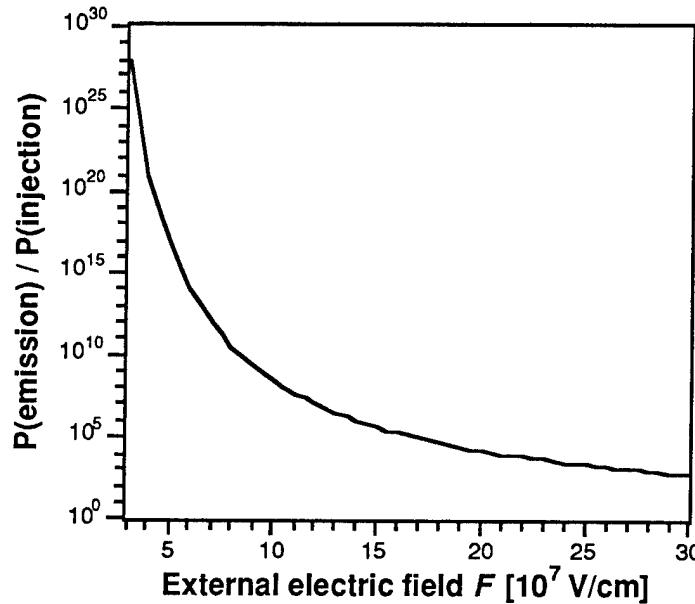


Figure 4. Ratio of the tunneling probability for the injection barrier at the Mo-diamond interface and the emission barrier at the diamond-vacuum interface. Calculations based on the WKB approximation.

at the Mo-diamond interface, compared to the uncoated Mo-vacuum interface, was determined not to be the cause for the enhancement because the applied electric field would be decreased at this interface by the dielectric constant of diamond. A negative electron affinity surface of intrinsic diamond was not the cause of enhancement under typical applied field strengths either. Even the transmission probability for a positive electron affinity surface is negligible compared to the transmission probability for the injection interface. The injection barrier, for intrinsic diamond, poses a more significant limitation to the emission process than the low positive or negative electron affinity at the diamond-vacuum interface. Therefore, this research indicated that enhanced emission from diamond is likely due to the field enhancement at the Mo-diamond interface.

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F. References

1. I. Brodie and P. R. Schwoebel, Proceeding of the IEEE **82**, 1006 (1994).
2. T. Asano, Y. Oobuchi and S. Katsumata, J. Vac. Sci. Technol. **B 13**, 431 (1995).
3. V. V. Zhirnov, E. I. Givargizov and P. S. Plekhanov, J. Vac. Sci. Technol. **B 13**, 418 (1995).
4. L. S. Pan, Mat. Res. Symp. Proc. **416**, 407 (1995).
5. C. Nützenadel, O. M. Küttel, O. Gröning and L. Schlapbach, Appl. Phys. Lett. **69**, 2662 (1996).
6. R. E. Thomas, T. P. Humphreys, C. Pettenkofer, D. P. Malta, J. B. Posthill, M. J. Mantini, R. A. Rudder, G. C. Hudson and R. J. Markunas, Mat. Res. Symp. Proc. **416**, 263 (1996).
7. P. K. Baumann and R. J. Nemanich, Mat. Res. Symp. Proc. **416**, 157 (1996).
8. R. Schlesser, M. T. McClure, W. B. Choi, J. J. Hren and Z. Sitar, Appl. Phys. Lett. **70**, 1596 (1997).
9. M. W. Geis, J. C. Twitchell, N. N. Efremow, K. Krohn and T. M. Lyszczarz, Appl. Phys. Lett. **68**, 2294 (1996).
10. A. F. Myers, Ph. D. thesis, North Carolina State University, 1996.
11. A. F. Myers, W. B. Choi, J. J. Cuomo and J. J. Hren, *Microscopy and Microanalysis 1996* 1996, Minneapolis, MN, USA, edited by G. W. Bailey, J. M. Corbett, R. V. W. Dimlich, J. R. Michael and N. J. Zaluzec, (San Francisco Press, Inc., 1996) p. 958.
12. I. Brodie and C. A. Spindt, Advances in Electronics and Electron Physics **83**, 1 (1992).
13. D. Nicolaescu, J. Vac. Sci. Technol. **B13**, 531 (1995).
14. K. L. Jensen and E. G. Zaidman, J. Vac. Sci. Technol. **B13**, 511 (1995).
15. K. L. Jensen, J. Vac. Sci. Technol. **B13**, 516 (1995).
16. R. C. Weast, *CRC Handbook of Chemistry and Physics*, 64th edition (CRC Press, Inc., Boca Raton, FL, Boca Raton, 1983) p. E-91.
17. D. E. Gray, *American Institute of Physics Handbook*, 3rd edition (McGraw-Hill Book Company, New York, 1972) p. 9-173.
18. E. H. Rhoderick and R. H. Williams, *Metal-Semiconductor Contacts*, 2 edition (Clarendon Press, Oxford, 1988) p. 231.
19. G. Davies, *Properties and Growth of Diamond*, (Short Run Press Ltd., Exeter, 1994) 437.

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